

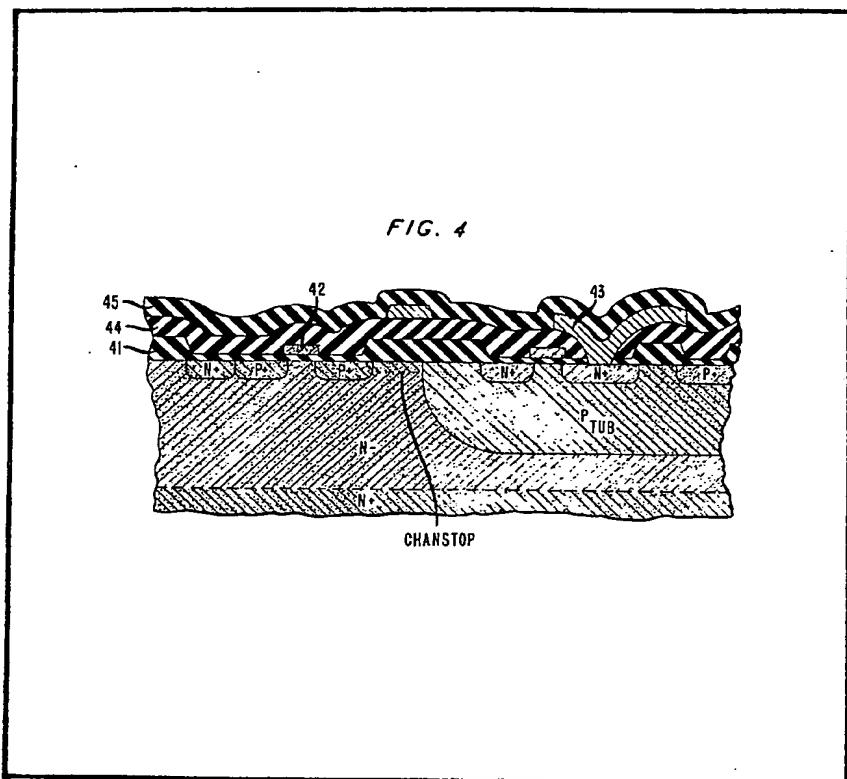
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(71) Applicant
Western Electric
Company Incorporated,
(USA—New York),
222 Broadway,
New York,
N Y 10038,
United States of America
(72) Inventor
Theodore Frank Retajczyk
(74) Agent and/or address for
service
K. G. Johnston,
Western Electric
Company Limited,
5 Mornington Road,
Woodford Green,
Essex,
IG8 0TU

(54) Polymeric films for electronic circuits

(57) Electronic circuits are described in which polysiloxane films 45 made by plasma-induced polymerization of at least one alkylalkoxysilane, in which the alkyl and alkoxy groups contain 1—3 carbon atoms each, are used as protective and dielectric layers. Such layers are highly advantageous in that

they are chemically inert, exhibit excellent thermal stability and have low dielectric constant. Electronic circuits with these films may be processed at relatively high temperatures without damage and have minimum parasitic capacitances where conductor spacing is extremely small and access times are very short. The layers are particularly useful for high density, high frequency memory and logic circuits.



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FIG. 1

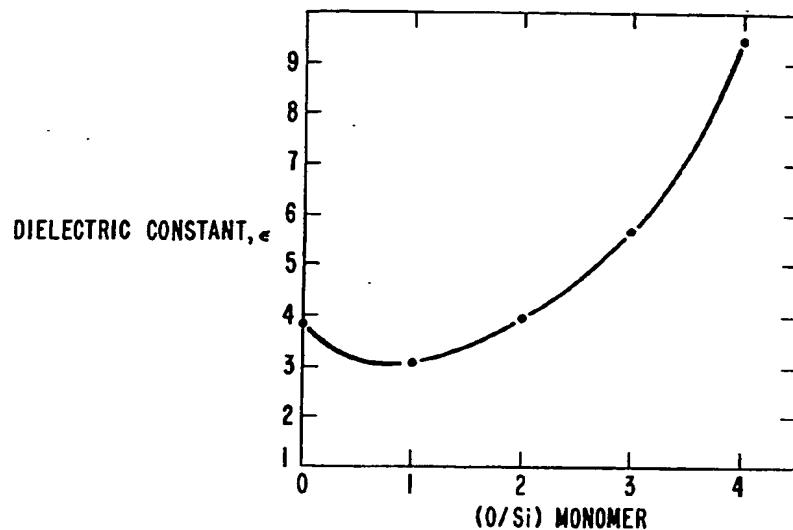
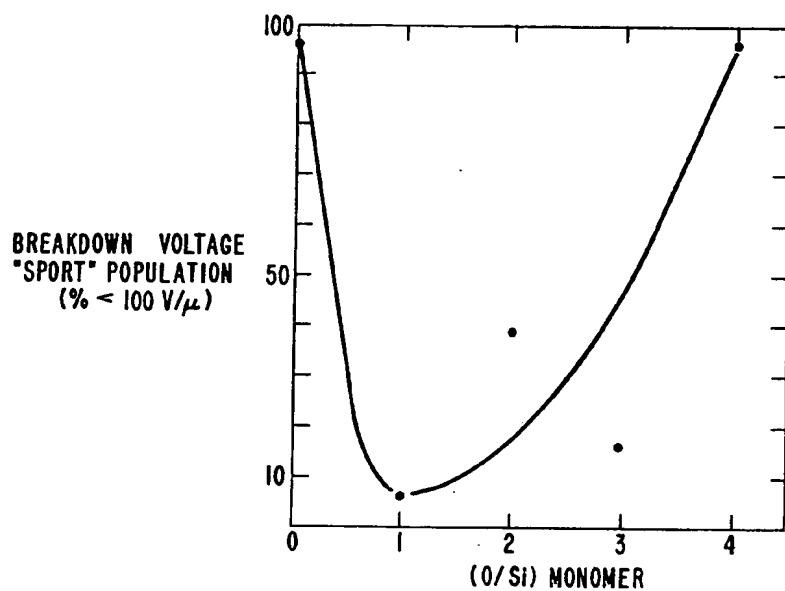


FIG. 2



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FIG. 3

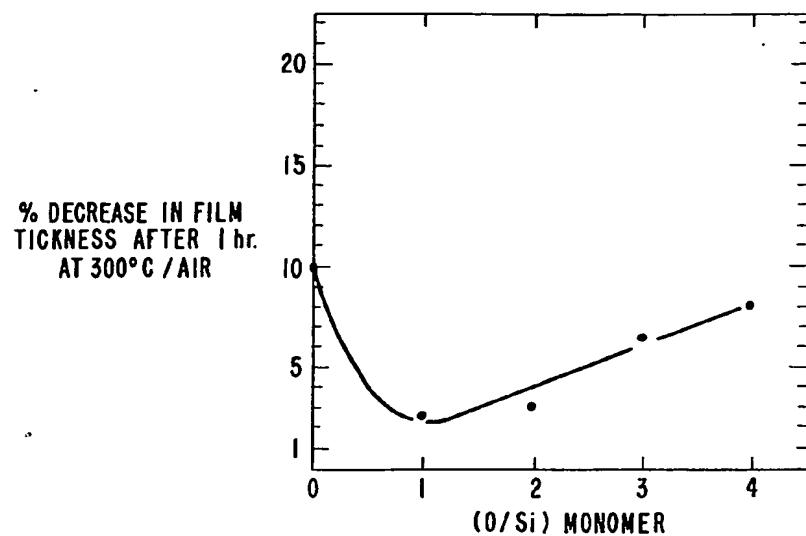
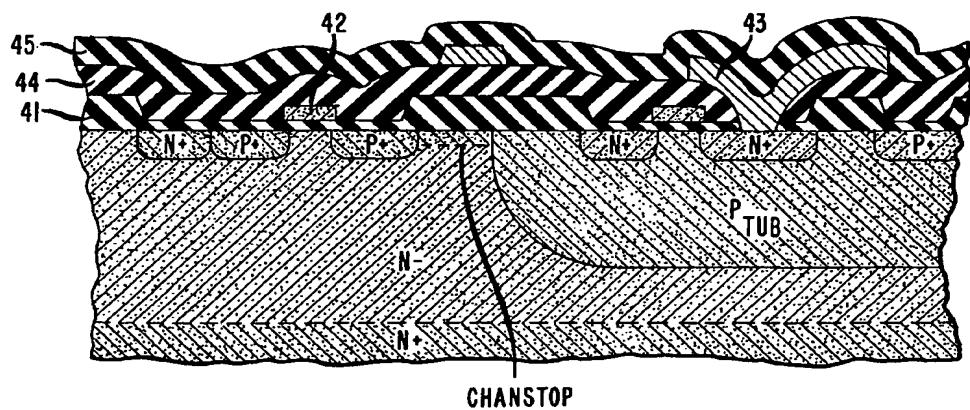


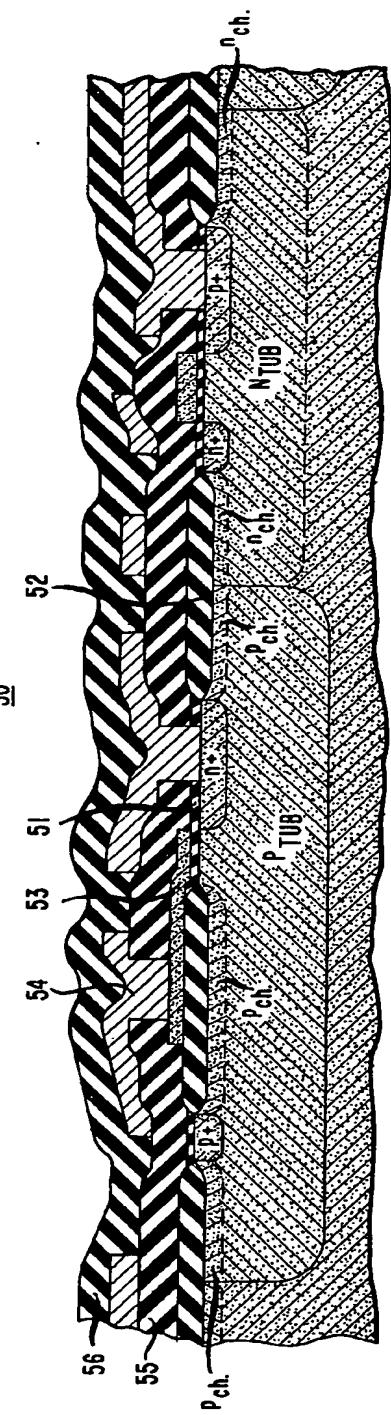
FIG. 4



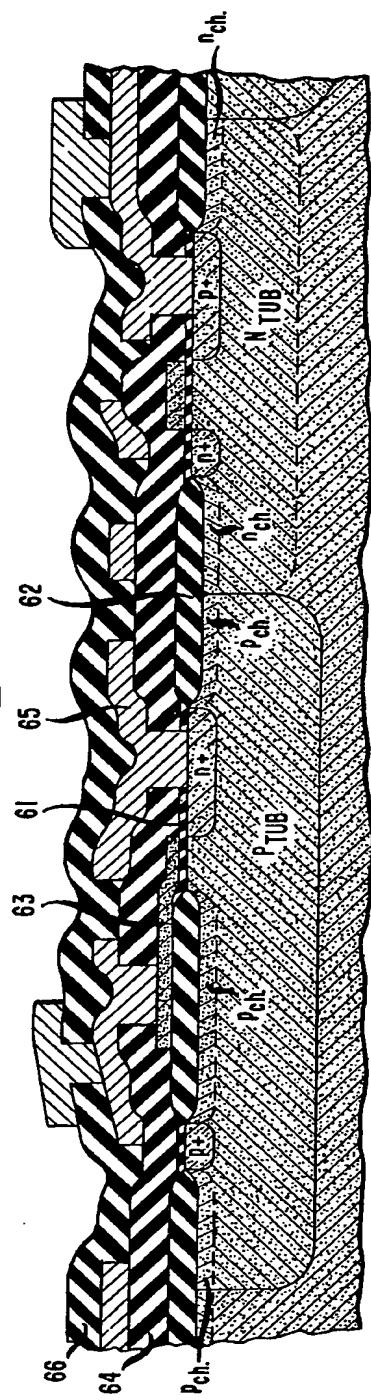
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SPECIFICATION

Polymeric films for electronic circuits

The invention involves electronic circuits with polymeric films used as insulator and dielectric layers.

The ever continuing advances in VLSI technology have led to greater packing density and shrinking design rules. This has created a need for new and improved dielectric materials for use in various device structures. For example, the close proximity of various conducting elements in the VLSI circuit has created a need for dielectric material of low dielectric constant so as to reduce parasitic capacitances. Also required is high dielectric strength because of the close approach of various conducting elements in the VLSI circuits. The use of two or more levels of metallization creates the need for dielectric material with other unique properties. For example, it is desirable in some cases that the dielectric be applied at a relatively low temperature so as to not adversely affect the multilevel circuit. In other cases, processing of these multilevel circuits often involves the use of relatively high temperatures to which the dielectric material must be stable. Also, the reduced feature sizes and higher applied voltages found in new VLSI devices may require new materials for classification and encapsulation.

Desirable properties for dielectric layers in use for VLSI circuits are low dielectric constants so as to minimize parasitic capacitances, high thermal stability so as to permit further processing of the circuit at high temperatures, relatively low application temperature so as to minimize damage to the circuit on application of the dielectric, high dielectric strength, good adherence, good film integrity (i.e., freedom from cracks) and chemical stability particularly to water and water vapor. Such a dielectric material would be extremely valuable and particularly for application to high density circuits because reduced parasitic capacitances would permit higher speeds and thermal stability would permit greater flexibility in processing such circuits.

A number of studies have been made of the use of polymer films in electronic circuits both as an insulator and as an encapsulating film and a passivating film. Most noteworthy of these are as follows: A. Szeto and D. W. Hess in a paper entitled "Correlation of Chemical and Electrical Properties of Plasma—Deposited Tetramethyl-silane Films", *Journal of Applied Physics*, 52 (2), 903 (1981), have studied the properties of tetra-methylsilane films of interest in electric circuit fabrication. Similar studies have been carried out for polymer films made by plasma induced polymerization of hexamethyldisiloxane. These studies have been reported in the following papers: M. Maisonneuve et al, *Thin Solid Films*, 44, pp.209—216 (1977); M. Aktik et al, *Journal of Applied Physics*, 51 (9), pp. 5055—5057 (1980); M. Maisonneuve et al, *Thin Solid Films*, 33, pp. 35—41 (1976); and J. E. Klemberg-Sapieha,

65 *Applied Physics Letters*, 37 (1), pp. 104—105 (1980).

According to the present invention there is provided a semiconductor electrical apparatus comprising semiconductor material and conducting elements, characterized in that the apparatus further comprises polysiloxane film made by plasma-induced polymerization of at least one alkylalkoxysilane with the alkyl and alkoxy groups containing up to 3 carbon atoms.

70 A preferred embodiment of the invention provides an electrical circuit in which at least part of a surface of the circuit is covered with a plasma-deposited polysiloxane film in which the monomer is an alkylalkoxysilane. The alkyl and alkoxy groups should not contain more than three carbon atoms. Typical examples are trimethylmethoxysilane, dimethyldimethoxysilane, tri-ethylethoxysilane, etc. Preferred is the monomer trimethylmethoxysilane because of low dielectric

75 constant, high breakdown voltage, low film stresses and a reasonable degree of thermal stability and high hydrophobicity. The polymer film is useful for a large variety of electrical circuits, high frequency, low frequency, direct current, etc. Typically, a circuit comprises a substrate, conductor elements, input connections, output connections, etc. These films are highly advantageous where at least some of the conductor spacings are very low (i.e., of the order

80 of 2 microns or less and circuit frequencies (or corresponding access times) are very high (i.e., greater than 5 MHz). It is also highly advantageous where aluminum metallization is used or other metallization where thermal cycling

85 is required.

90 For a better understanding of the Invention, reference is made to the accompanying drawings in which:—

95 Fig. 1 shows a graph of same data on dielectric constant for polysiloxane films made from a variety of alkylalkoxysilanes;

100 Fig. 2 shows a graph of same data on breakdown voltage for polysiloxane films made from a variety of alkylalkoxysilanes;

105 Fig. 3 shows a graph of same data on thermal effect on film thickness for polysiloxane films made from a variety of alkylalkoxysilanes;

110 Fig. 4 shows a cross-sectional view of a portion of a typical integrated circuit showing certain features of such circuit including a cap layer made of a polysiloxane material;

115 Fig. 5 shows a cross-sectional view of a portion of a more complex integrated circuit with a cap material made in accordance with an embodiment of the invention; and

120 Fig. 6 shows a cross-sectional view of a portion of an integrated circuit in which polysiloxane is used as an interlevel dielectric to separate two levels of aluminum metallization.

125 It has been discovered, that certain silicon-containing polymers made by plasma-polymerization of certain oxygen-containing organo-silicon compounds yield polysiloxane polymer films with unusually good properties for use in

integrated circuits, especially VLSI-type circuits with high densities of circuit elements and short access times (typically less than 10^{-6} or 10^{-7} seconds). The films can be of benefit to a large variety of circuits. Such circuits preferably contain semiconductor material (e.g., silicon, germanium, gallium arsenide, etc.), substrate (often also the semiconducting material), conductor elements (e.g., aluminum) and various doped regions.

Various alkylalkoxysilanes may be used as monomers provided the number of carbons in the alkyl group and the number of carbons in the alkoxy group does not exceed three. Generally up to 20 percent of substances outside this class may be used to alter the properties of the polymer (fillers, cross-linking agents), property modifiers of various kinds, etc.). Although for most applications, the monomer should mainly consist of the class described above. More than one alkylalkoxysilane may be used as the monomer although ordinarily only a single monomer is used. Preferred are alkylalkoxysilane monomers in which the alkyl groups are methyl groups. Most preferred is the trimethylmethoxysilane monomer because the resulting polymer has very low dielectric constant, high thermal stability and excellent adherence properties. These properties are highly advantageous for many circuit applications for a number of reasons. Dielectric constant often limits access times and clock frequencies in many memory and logic circuits. Thermal cycling is often required in the fabrication of integrated circuits, especially those containing aluminum conducting elements. Adherence is especially important in encapsulation applications and where multiple conducting layers are used. The thickness of layers may vary over large limits (often as thin as $0.05 \mu\text{m}$) and usually depends on the particular application. Typical is from 0.2 to 100 micrometers. For many circuit applications, thicknesses from 0.5 to 10 micrometers usually yield satisfactory results. For many applications, the film should be as thin as possible without incurring any deleterious effects. For example, in some circuit applications, it is desirable to minimize thickness so as to minimize capacitance effects but maintain sufficient thickness to prevent voltage breakdown and diffusion through the film. Often optimum thickness from this point of view occurs between 0.5 and 2 micrometers.

A plasma discharge procedure is used to produce the polymer film from the monomer. Satisfactory results are obtained from conventional procedures described in detail in a number of books and references. Typical books are *Technique and Applications of Plasma Chemistry*, edited by J. R. Hollab and A. T. Bell (Wiley-Interscience, New York, 1974), especially M. Millard, Chapter 5, page 177 and *Plasma Polymerization*, edited by M. Shen and A. T. Bell, ACS Symposium Series No. 108 (American Chemical Society, Washington, D.C., 1979).

The particular apparatus used in the experiments described below is typical of

equipment used for plasma-induced polymerization. The films were deposited in a parallel plate, 40 cm diameter, radial flow reactor. The electrode gap was about 2 cm and the operating frequency about 13.56 MHz. Both the RF excited electrode and the grounded (susceptor) plates were water cooled at a temperature of about 35—40 degrees C. The reagents were obtained commercially and were used without further preparation. All the chemicals used were liquids at room temperature and flow rates were adjusted using a needle valve to give a system pressure of 50 millitorr in the absence of a plasma. The pressure without the introduction of monomer was about 5 millitorr. The plasma was operated at about 50 volts and films were deposited on a precleaned silicon substrate mounted on the bottom grounded plate. Film thickness and refractive index were determined ellipsometrically with an Ellipsometer II (Applied Materials Corp), with film thicknesses cross-checked using a Nanospec (Nanometrics). Film stoichiometry was determined from Rutherford backscattering measurements. Film stress measurements were obtained using an optically-levered laser beam method wherein stress is determined from changes induced in the radius of curvature of a substrate after a film is deposited. Contact angle measurements were made using a Rame-Hart goniometer. Electrical properties were obtained by first evaporating Al dots on the films and, in the case of the dielectric constant determination, obtaining a C—V curve and measuring the capacitance in accumulation. Breakdown voltage measurements were obtained by probing 100 dots per film and measuring the voltage required to pass $2 \mu\text{A}$ of current.

Various monomers were used in these experiments, corresponding to O/Si mole ratios from zero (tetramethylsilane) or 1 (trimethylmethoxysilane) to 4 (tetramethoxysilane). The experiments showed that deposition rate is essentially the same (about 60 Angstroms per minute) for O/Si ratios from one to four. Film stress is essentially zero for O/Si ratios of zero and increases from about 3 to 5×10^8 dynes per square centimeter as O/Si ratios increase from one to four. Such stresses are quite reasonable for most applications including use in circuit applications. The polysiloxane polymers become less hydrophobic as the ratio O/Si increases from one to four with both tetramethylsilane and trimethylmethoxysilane most hydrophobic. Index of refraction decreases modestly with increasing ratio of O/Si from 0 to 4.

Of particular significance is the dielectric behavior of the film as a function of film composition. Fig. 1 shows a graph of dielectric constant versus film composition (in terms of monomer starting material). As stated above, low dielectric constant is highly advantageous in modern circuit applications. Dielectric constant is a minimum for O/Si ratio of one (corresponding to

the monomer trimethylmethoxysilane). Largely because of this low dielectric constant and other good properties of this polymer, the polymer resulting from plasma-induced polymerization of 5 trimethylmethoxysilane is most preferred.

The dielectric strength of the films were also measured. The dielectric strength was quite low for O/Si equal to 0 and 4. The average values were less than 100 volts per micrometer.

10 However, for O/Si ratio 1 and 3 (trimethylmethoxysilane and methyltrimethoxysilane, respectively), the breakdown voltage averages in excess of several hundred volts per micrometer.

A convenient way of evaluating the breakdown 15 characteristics of a film is to plot the "sport" population against the monomer composition. The "sport" population is the percent of dots probed that have breakdown voltages less than 100 volts per micrometer. Such data are shown in 20 Fig. 2 for various starting monomers. The particularly low values for O/Si ratios of 1 and 3 are highly advantageous in applications involving electrical circuits. The other O/Si ratios may be higher due to softness of the films and the probe 25 used in the measurements.

The thermal properties of several polysiloxane 30 films were also examined. This was done by exposing the film to a temperature of 300 degrees C for one hour in air and measuring the percent reduction in film thickness. The results of these 35 experiments are given in Fig. 3. Here, the percent reduction in thickness is plotted as a function of the ratio of O/Si of the monomer used. Although all the polymer films exhibit excellent thermal stability, the thermal stability of the polymer film made from trimethylmethoxysilane is especially good. The thickness was only reduced by about 2.5 percent after being exposed to the heat treatment described above.

40 Although all of the polymer films made from alkylalkoxysilane monomers exhibit excellent properties particularly for electronic applications, the polymer films made from trimethylmethoxysilane exhibit exceptionally good properties for 45 such applications. The dielectric constant and film stress are minimal or near minimal, while properties such as hydrophobicity, dielectric strength and thermal stability are maximum or near maximum. Additional experiments showed 50 that polymer films made by plasma-induced polymerization of trimethylmethoxysilane has excellent adhesion as evidenced by the Scotch tape pull test and surviving a patterning process on a topographical surface. The film is readily 55 patterned using a $CF_4 \pm O_2$ plasma but is quite resistant to an O_2 plasma. This permits plasma stripping of resist in the presence of the polysiloxane film. The thermal stability was particularly impressive as evidenced by the fact 60 that even at 450 degrees C in the presence of forming gas or nitrogen, the film contracts only a few percent.

Fig. 4 shows a cross-sectional view of a typical 65 integrated circuit 40 with various features as labeled (such as p^+ channels, n^+ channels, etc.).

The circuit is conveniently described as a CMOS (Complementary Metal Oxide Semiconductor) circuit with a single tub single polysilicon structure exhibiting five micrometer design rules.

70 The exact features of the integrated circuit are not critical to understanding the invention and will be described only briefly. The substrate of the circuits is made of relatively heavily n doped silicon (typically phosphorus doped in the concentration 75 range of roughly 10^{18} atoms per cubic centimeter). This region is marked n^+ in the diagram. A lighter-doped region covers the n^+ region (marked n^-) and various other regions are marked such as P_{TUB} regions, n^+ channels and p^+ 80 channels. The CHANSTOP region is used to electrically isolate one region from another. An oxide region 41 is also part of the circuit. This oxide is usually SiO_2 and is often called a field oxide or FOX region. A polysilicon region 42 and 85 aluminum region 43 are also shown as well as a glass region 44 (usually phosphorus glass). The entire circuit is covered with a layer of plasma-polymerized polysiloxane 45. Usually the thickness varies between 0.5 and 2 micrometers.

90 Fig. 5 shows a side view of a more complex CMOS circuit 50 with P_{TUB} and N_{TUB} as well as p^+ type channels (p_{ch}) and n -type channels (n_{ch}). There are also regions of heavy p -type doping (p^+) and heavy n -type doping (n^+). Certain regions 95 have very thin oxide layers 51 usually made of SiO_2 and some thicker oxide layers 52 (again usually SiO_2) often referred to as field oxide or FOX. There is also a layer of $TaSi_2$ 53 (often polycrystalline silicon is used in the same capacity) 100 and various conducting layers 54 usually made of aluminum. Layers of phosphorus glass 55 are also used in the structure. As a capping layer 56, a polysiloxane layer is put down by plasma-induced polymerization of trimethylmethoxysilane over the 105 entire structure. The film is used as a protective layer and is usually about one micrometer thick.

Fig. 6 shows a somewhat more complex structure 60 with many of the features shown in Fig. 6 including gate oxide 61, field oxide 62, 110 $TaSi_2$ layer 63, phosphorus glass layer 64 and aluminum layer 65. Also shown is the polysiloxane layer 66 covering a large portion of the circuit. A particular difference between this circuit and the circuit shown in Fig. 5 is the use of a top 115 aluminum metal layer to selectively contact a bottom aluminum metal layer. Here, the polysiloxane is used not only as an encapsulating layer but also as an interlevel dielectric to separate the top level of aluminum from the rest of the circuit.

120 Claims

1. A semiconductor electrical apparatus comprising semiconductor material and conducting elements, characterized in that the apparatus further comprises polysiloxane film made by plasma-induced polymerization of at least one alkylalkoxysilane with the alkyl and alkoxy groups containing up to 3 carbon atoms.

2. Apparatus according to claim 1, wherein the alkyl group is a methyl group.

3. Apparatus according to claim 2, wherein the alkoxy group is a methoxy group.
4. Apparatus according to claim 3, wherein the alkylalkoxysilane is trimethylmethoxysilane.
5. Apparatus according to claim 1, wherein the conducting elements comprise aluminum.
6. Apparatus according to claim 1, wherein the thickness of the polysiloxane film is between 0.05 and 100 micrometers.
- 10 7. Apparatus according to claim 6, wherein the thickness of the polysiloxane film is between 0.5 and 10 micrometers.
8. Apparatus according to claim 7, wherein the thickness of the polysiloxane film is between 0.5 and 2.0 micrometers.
- 15 9. Apparatus according to claim 1, wherein at least two of the conducting elements have spacing less than two microns.
10. Apparatus according to claim 1, wherein 20 the semiconducting material is selected from silicon, gallium arsenide and germanium.
11. Apparatus according to claim 10, wherein the semiconducting material is silicon.
12. Apparatus according to claim 11, wherein 25 the semiconducting electrical apparatus is a memory circuit.
13. Apparatus according to claim 11, wherein the semiconducting electrical apparatus is a logic circuit.
14. Semiconductor electrical apparatus 30 substantially as hereinbefore described with reference to any one of the Figs. of the accompanying drawings.

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